

Template Synthesis of Nano-Structured Carbons

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The template carbonization method consists of the carbonization of an organic compound in nanospace of a template inorganic substance and the liberation of the resulting carbon from the template. So far various types of unique carbon materials have been synthesized using this method. For instance, when an anodic aluminum oxide (AAO) film whose porosity consists of myriads of parallel and uniform nanochannels was used as a one-dimensional template, carbon nanotubes can be prepared by the following procedure. Pyrolytic carbon deposition on the channel wall of an AAO film was carried out with exposing the film to hydrocarbon gas at high temperature. The carbon was then liberated from the film by dissolving the alumina template with HF or NaOH solution. The resulting carbon comprises only uniform multiwalled carbon nanotubes and, the length and diameter of the nanotubes are controllable by changing the length and the inner diameter of the channels

in the AAO film, respectively [1]. By using this template technique, NiFe alloy or Ni(OH)₂ filled uniform carbon nanotubes can easily be fabricated (Fig. 1) [2, 3]. It should be noted that no metal was observed on the outside walls of the tubes. The test tube like carbon (carbon nano test tubes; CNTTs) prepared by this technique was found to be dispersible in water without any post treatment [4]. Surprisingly, such water dispersibility can be kept even after the loading of magnetic metal into the tube cavities, and the tubes are responsive to a magnetic field (Fig. 2) [5]. Not only inorganic compounds but also dye [6] and, even DNA molecules, can be introduced into the cavities of CNTTs. For instance, the open ends of CNTTs could be plugged with polystyrene and their water-dispersibility was still kept. Such water-dispersible, magneto-responsive and plugged CNTTs have great potential as carriers for magnetic delivery system in which the carriers are guided to a target tissue by an external applied magnetic field.

In addition to this one-dimensional approach, unique microporous carbon can be prepared by the template technique using zeolite Y (Fig. 3). The resulting microporous carbons are characterized by their regular ordering, originating from the regularity of the parent zeolite [7]. When the synthesis conditions were optimized, the specific surface area and the micropore volume of the zeolite-templated carbon reach more than 4000 m²/g and 1.8 cm³/g, respectively. Furthermore, the carbon possesses only micropores and its pore size distribution is quite narrow. Despite these unique features, its molecular structure had

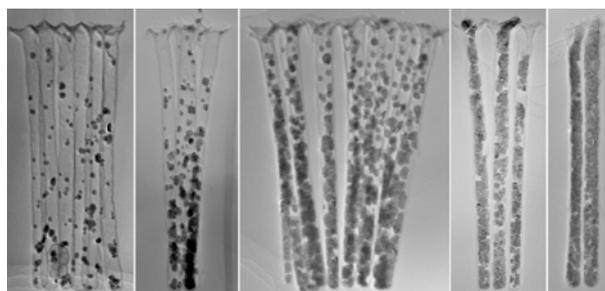


Fig. 1 Filling of NiFe alloy into carbon nano test tubes in a controlled manner.

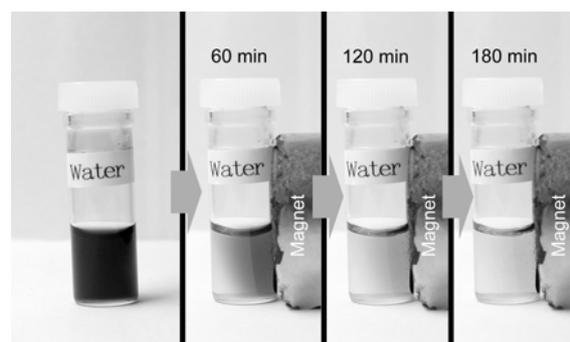


Fig. 2 Magneto-responsive behavior of NiFe-loaded carbon nano test tubes dispersed in water.

remained totally unknown. Lattice fringes of graphene sheets in this carbon can never be observed even with high-resolution transmission electron microscopy, although ^{13}C NMR detected

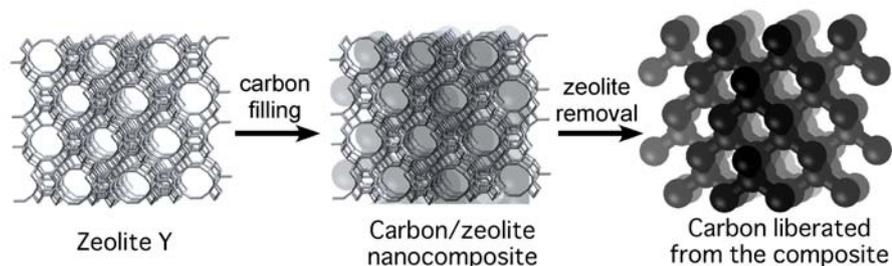


Fig. 3 Synthesis process of ordered microporous carbon using zeolite Y as a template.

only sp^2 carbon atoms in this material. Very recently, using Raman spectroscopy and a semi-empirical molecular orbital (MO) theory, together with previously obtained analysis results, we have proposed an approximate molecular model for the present carbon, which consists of cross-linked single nanographene sheets where each graphene is forced to be artificially curved by the steric hindrance imposed by the zeolite nanochannels [8]. With the curved and ordered single graphene layers, this new form of carbon should possess many peculiar properties as compared to porous carbons with stacked graphene structure. Furthermore, due to the extremely large surface area and surprisingly uniform micropore structure, this carbon is quite promising for such applications as adsorbent for hydrogen storage [9] and as an electrode for electric double layer capacitor (EDLC) [10]. For example, ZTC exhibited as high a hydrogen uptake as 2.2 wt% at 34 MPa. Moreover, only by loading a small amount of Pt nanoparticles (ca. 0.2 wt%) onto ZTC, hydrogen uptake capacity was increased from 0.87 wt % to 0.95 wt% at 10 MPa. The increase of hydrogen uptake capacity by Pt-loading can be ascribed to hydrogen spillover through the supported Pt nanoparticles to the carbon surface. As for the EDLC performance, ZTC showed an excellent rate performance; ZTC kept as high as 81% of its initial capacitance (137 F/g at 0.05 A/g) even at as large a current density as 20 A/g, under which conditions the capacitances of all other conventional activated carbons became much lower than that of ZTC.

References

- [1] T. Kyotani, L.-F. Tsai and A. Tomita, *Chem. Mater.*, **7** (1995) 1427, *Chem. Mater.*, **8** (1996) 2109.
- [2] X.-H. Wang, H. Oriyasa, N. Inokuma, Q.-H. Yang, P.-X. Hou, H. Oshima, K. Itoh, T. Kyotani, *J. Mater. Chem.*, **17** (2007) 986.
- [3] H. Oriyasa, J. Karoji, K. Matsui, T. Kyotani, *Dalton Trans.*, **34** (2007) 3757.
- [4] H. Oriyasa, N. Inokuma, S. Okubo, O. Kitakami, T. Kyotani, *Chem. Mater.*, **18** (2006) 1036.
- [5] H. Oriyasa, N. Inokuma, S. Ittisanronnachai, X.-H. Wang, O. Kitakami, T. Kyotani, *Chem. Commun.*, (2008) 2215.
- [6] S. Ittisanronnachai, H. Oriyasa, N. Inokuma, Y. Uozu, T. Kyotani, *Carbon*, **46** (2008) 1361.
- [7] Z.-X. Ma, T. Kyotani, A. Tomita, *Chem. Commun.*, (2000) 2365, Z.-X. Ma, T. Kyotani, Z. Liu, O. Terasaki, A. Tomita, *Chem. Mater.*, **13** (2001) 4413.
- [8] H. Nishihara, Q.-H. Yang, P.-X. Hou, M. Unno, S. Yamauchi, R. Saito, J. I. Paredes, A. Martínez-Alonso, J. M.D. Tascón, Y. Sato, M. Terauchi, T. Kyotani, *Carbon*, **47** (2009) 1220.
- [9] H. Nishihara, P.-X. Hou, L.-X. Li, M. Ito, M. Uchiyama, T. Kaburagi, A. Ikura, J. Katamura, T. Kawarada, K. Mizuuchi, T. Kyotani, *J. Phys. Chem. C*, **113** (2009) 3189.
- [10] H. Nishihara, H. Itoi, T. Kogure, P.-X. Hou, H. Touhara, F. Okino, T. Kyotani, *Chem. Eur. J.*, **15** (2009) 5355.